

Velocity Autocorrelation and Harmonic Motion in Supercooled Nondiffusing Monatomic Liquids

Eric D. Chisolm, Brad E. Clements, and Duane C. Wallace
Theoretical Division
Los Alamos National Laboratory
Los Alamos, NM 87545

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Abstract

Studies of the many-body potential surface of liquid sodium have shown that it consists of a great many intersecting nearly harmonic valleys, a large fraction of which have the same frequency spectra. This suggests that a sufficiently supercooled state of this system, remaining in a single valley, would execute nearly harmonic motion. To test this hypothesis, we have compared $\hat{Z}(t)$, the normalized velocity autocorrelation function, calculated from MD simulations to that predicted under the assumption of purely harmonic motion. We find nearly perfect agreement between the two, suggesting that the harmonic approximation captures all essential features of the motion.

1 Introduction

Recent work by Wallace and Clements [1, 2] has uncovered several important properties of the many-body potential underlying the motion of liquid sodium systems. Specifically, it has been shown that (a) the potential surface consists of a large number of intersecting nearly harmonic valleys, (b) these valleys can be classified as symmetric (crystalline, microcrystalline, or retaining some nearest-neighbor remnants of crystal symmetry) or random, with the random

valleys vastly outnumbering the symmetric ones, (c) the frequency spectra of different random valleys are nearly identical (while those of the symmetric valleys vary widely), and (d) below 35 K the system remains in a single valley throughout the longest molecular dynamics (MD) runs that were performed. Results (a) through (c) verify predictions made by Wallace in his theory of liquid dynamics [3], which has been successfully applied to account for the high-temperature specific heats of monatomic liquids [4] and a study of the velocity autocorrelation function [5]. These four results together suggest that below 35 K the motion of the atoms in liquid sodium is purely harmonic to a high degree of approximation, again as predicted by Wallace in [3], and we would like to test this hypothesis further. One check is to compare the mean square displacement from MD with the prediction from purely harmonic motion, which is done in Fig. 12 of [1], where the two are found to agree closely. However, it would be more convincing if the theory could be shown to reproduce an entire scalar function calculated from MD (instead of just a single number), such as the normalized velocity autocorrelation function $\hat{Z}(t)$. That is the aim of this paper. We will show that purely harmonic motion of the atoms in a potential valley produces a $\hat{Z}(t)$ which matches that of MD calculations to within the calculations' accuracy; thus we will conclude that the motion of atoms in a nondiffusing supercooled liquid state is very nearly entirely harmonic. For completeness, in Sec. 2 we briefly review the calculation of $\hat{Z}(t)$ assuming harmonic motion, and in Sec. 3 we compare this result with MD. Finally, in Sec. 4 we make contact with work by others in this field, as well as comparing these results to Wallace's earlier effort [5] mentioned above.

2 Harmonic Theory

If an N -body system is moving in a potential valley, the potential can be expanded about the valley minimum with the resulting Hamiltonian

$$H = \sum_{Ki}' \frac{p_{Ki}^2}{2M} + \sum_{Ki,Lj}' \Phi_{Ki,Lj} u_{Ki} u_{Lj} + \Phi_A \quad (1)$$

where u_{Ki} is the i th component of the K th particle's displacement from equilibrium, p_{Ki} is the corresponding momentum, and the anharmonic term Φ_A contains all of the higher order parts of the expansion. The primed sum indicates that the sum is performed under the constraint that the center of

mass of the system is stationary. (As a result, the system has only $3N - 3$ independent degrees of freedom.) The matrix $\Phi_{Ki,Lj}$ is called the dynamical matrix of the system. If the valley is approximately harmonic, we can neglect Φ_A . If coordinates q_λ are defined by the relation

$$u_{Ki} = \sum_{\lambda} w_{Ki,\lambda} q_{\lambda} \quad (2)$$

where the $w_{Ki,\lambda}$ form a $3N \times 3N$ orthogonal matrix, satisfying

$$\sum_{Ki} w_{Ki,\lambda} w_{Ki,\lambda'} = \delta_{\lambda\lambda'}, \quad (3)$$

then the Hamiltonian in these new coordinates is

$$H = \sum_{\lambda} \frac{p_{\lambda}^2}{2M} + \sum_{Ki,Lj} ' \sum_{\lambda\lambda'} w_{Ki,\lambda} \Phi_{Ki,Lj} w_{Lj,\lambda'} q_{\lambda} q_{\lambda'} \quad (4)$$

where the p_{λ} are the momenta conjugate to the q_{λ} . Now one can always choose the $w_{Ki,\lambda}$ to diagonalize $\Phi_{Ki,Lj}$, so that

$$\sum_{Ki,Lj} w_{Ki,\lambda} \Phi_{Ki,Lj} w_{Lj,\lambda'} = M \omega_{\lambda}^2 \delta_{\lambda\lambda'}. \quad (5)$$

(This equation defines the frequencies ω_{λ} in terms of the eigenvalues of $\Phi_{Ki,Lj}$.) With this choice, the Hamiltonian becomes

$$H = \sum_{\lambda} \left(\frac{p_{\lambda}^2}{2M} + \frac{1}{2} M \omega_{\lambda}^2 q_{\lambda}^2 \right). \quad (6)$$

Three of the ω_{λ} are zero; these modes correspond to uniform motion of the center of mass. Since we have restricted the center of mass position and velocity to zero, these modes are not excited. The classical equations of motion for the remaining modes are solved by

$$q_{\lambda}(t) = a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}), \quad (7)$$

or, returning to the original coordinates,

$$u_{Ki}(t) = \sum_{\lambda} w_{Ki,\lambda} a_{\lambda} \sin(\omega_{\lambda} t + \alpha_{\lambda}), \quad (8)$$

with the understanding that the sum on λ ranges from 1 to $3N - 3$. The velocities of the particles are

$$v_{Ki}(t) = \sum_{\lambda} w_{Ki,\lambda} \omega_{\lambda} a_{\lambda} \cos(\omega_{\lambda} t + \alpha_{\lambda}). \quad (9)$$

We compute the $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ in $Z(t)$ by calculating $\mathbf{v}_K(t) \cdot \mathbf{v}_K(0)$, summing over K and dividing by $N - 1$ (remember that only $3N - 3$ coordinates are independent), and averaging over the amplitudes a_{λ} and phases α_{λ} . Thus

$$\begin{aligned} Z(t) &= \frac{1}{3} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \\ &= \frac{1}{3N - 3} \sum_{Ki} \sum_{\lambda\lambda'} w_{Ki,\lambda} w_{Ki,\lambda'} \omega_{\lambda} \omega_{\lambda'} \langle a_{\lambda} a_{\lambda'} \rangle \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda'}) \rangle \\ &= \frac{1}{3N - 3} \sum_{\lambda\lambda'} \delta_{\lambda\lambda'} \omega_{\lambda} \omega_{\lambda'} \langle a_{\lambda} a_{\lambda'} \rangle \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda'}) \rangle \\ &= \frac{1}{3N - 3} \sum_{\lambda} \omega_{\lambda}^2 \langle a_{\lambda}^2 \rangle \langle \cos(\omega_{\lambda} t + \alpha_{\lambda}) \cos(\alpha_{\lambda}) \rangle \\ &= \frac{1}{6N - 6} \sum_{\lambda} \omega_{\lambda}^2 \langle a_{\lambda}^2 \rangle \cos(\omega_{\lambda} t). \end{aligned} \quad (10)$$

By the equipartition theorem,

$$\left\langle \frac{1}{2} M \omega_{\lambda}^2 q_{\lambda}^2 \right\rangle = \frac{1}{2} kT \quad (11)$$

for any nonzero ω_{λ} , from which it follows that

$$\langle a_{\lambda}^2 \rangle = \frac{2kT}{M\omega_{\lambda}^2}, \quad (12)$$

so

$$Z(t) = \frac{1}{3N - 3} \frac{kT}{M} \sum_{\lambda} \cos(\omega_{\lambda} t). \quad (13)$$

Notice that $Z(0) = kT/M$, so $\hat{Z}(t)$ defined by

$$Z(t) = Z(0) \hat{Z}(t) \quad (14)$$

is given in this theory by

$$\hat{Z}(t) = \frac{1}{3N-3} \sum_{\lambda} \cos(\omega_{\lambda} t). \quad (15)$$

This is the result we wish to compare with MD.

To do so, we need the frequencies ω_{λ} , which are related to the eigenvalues of the dynamical matrix $\Phi_{Ki,Lj}$ as indicated in Eq. (5). These were evaluated for five separate random valleys in [1] by quenching all the way down to a valley minimum and diagonalizing $\Phi_{Ki,Lj}$ there; as pointed out in Sec. 1, these eigenvalues were found to be independent of the specific random valley chosen. All five sets of eigenvalues are shown in Fig. 7 of [1], and we picked one set at random to use in performing the sum in Eq. (15); the other sets produce identical graphs of $\hat{Z}(t)$.

We can also use the set of eigenvalues to reconstruct the density of frequencies $g(\omega)$; the results are shown in Fig. 1. Note that we do not actually integrate over this $g(\omega)$ to evaluate $\hat{Z}(t)$ below; we directly sum over the given set of frequencies as indicated in Eq. (15). The Figure is provided only to convey a sense of the shape of the frequency distribution. Also note that this $g(\omega)$ is determined from fully mechanical considerations; as a result, it is not temperature-dependent as are the frequency spectra used in Instantaneous Normal Mode (INM) studies [6, 7, 8, 9, 10]. We will expand on this point in the Conclusion.

3 Comparison with MD

The MD setup used to calculate $\hat{Z}(t)$ to compare with Eq. (15) is essentially that described in [1]: N particles interact through a potential that is known to reproduce accurately a wide variety of experimental properties of metallic sodium (see discussion in [1] for details). The two significant changes are that we used $N = 500$ for all runs and that the MD timestep was reduced to $\delta t = 0.2t^*$, where $t^* = 7.00 \times 10^{-15}$ s is the natural timescale defined in [1]. (The system's mean vibrational period $\tau = 2\pi/\omega_{\text{rms}}$, where the rms frequency ω_{rms} is calculated in [1], is approximately $300\delta t$.) We cooled the sodium sample to 22.3 K and 6.69 K, and then we ran each at equilibrium to collect velocities $\mathbf{v}_K(t)$ to be used to calculate $Z(t)$ by the formula

$$Z(t) = \frac{1}{3N} \sum_K \frac{1}{n+1} \sum_{t'=0}^n \mathbf{v}_K(t+t') \cdot \mathbf{v}_K(t'). \quad (16)$$

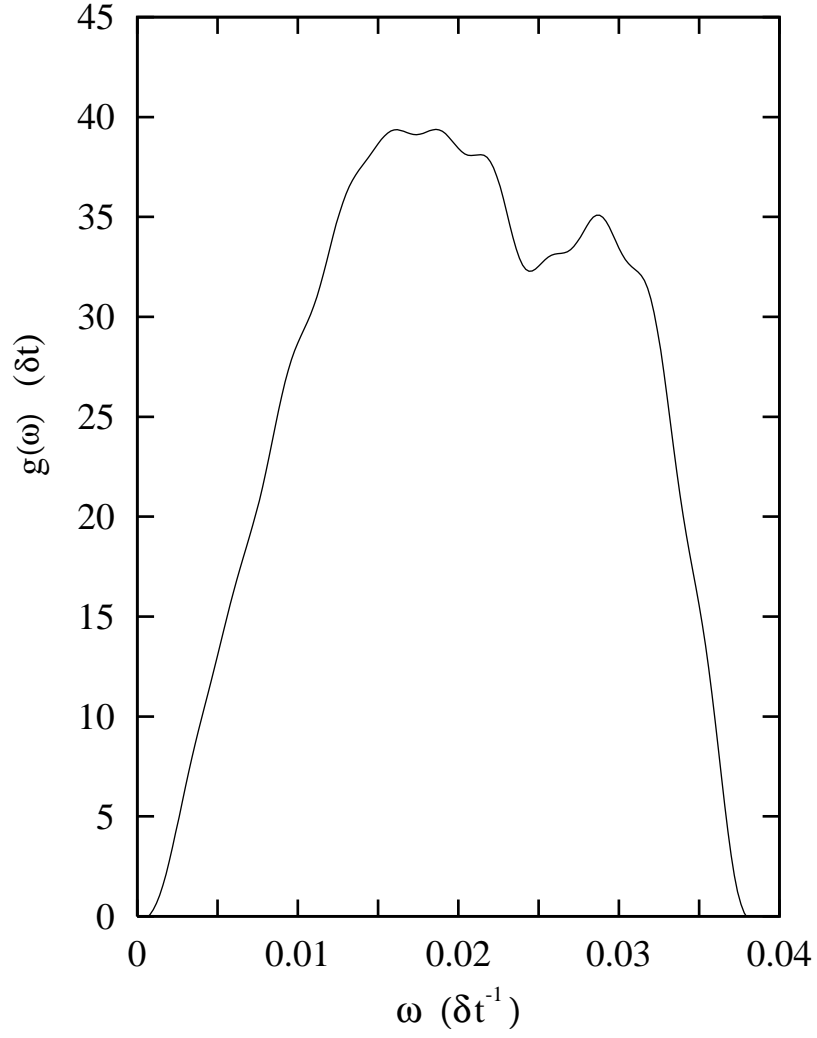


Figure 1: $g(\omega)$ constructed from one of the five sets of frequencies in Fig. 7 of [1]. This same set of frequencies is used to calculate $\hat{Z}(t)$ from Eq. (15).

We then divided by $Z(0)$ to obtain $\hat{Z}(t)$. The number n was chosen as large as possible without running beyond the data calculated in the MD run. We know that at these temperatures the sodium is nondiffusing for two reasons: Both temperatures are below the 35 K threshold [1], and $\hat{Z}(t)$ from either MD run (shown below in Fig. 2) integrates to zero, yielding zero diffusion coefficient.

The formula above may fail to produce reliable values of $\hat{Z}(t)$ for three reasons. First, the number of data points in the time average may be too small; if the MD simulation is run out to time t_{\max} , then for a given value of t in Eq. (16), the maximum possible value of the upper limit n is $t_{\max} - t$. Thus we require $t_{\max} \gg t$; we have chosen $t_{\max} = 50,000$ timesteps and we have calculated $\hat{Z}(t)$ only to $t = 1000$. To ensure that this value of t_{\max} is large enough, we also performed MD runs out to 200,000 timesteps and calculated $\hat{Z}(t)$ from them; the differences from the 50,000 timestep result were of order 10^{-3} . Hence we are confident that 50,000 timesteps is enough if we calculate $\hat{Z}(t)$ to only 1000 timesteps. Second, it is possible that reducing the timestep (thus increasing the accuracy of the simulation) might improve the accuracy of $\hat{Z}(t)$. To test this, we performed another MD run with δt reduced to $0.05t^*$, keeping the “real” time of the run the same; this also produced differences in $\hat{Z}(t)$ of order 10^{-3} . Thus we are sure that our timestep is small enough. Finally, there is the possibility of finite size effects. Since the MD system has periodic boundary conditions, an acoustic wave sent out from the system at $t = 0$ could propagate across the simulation region and return to its point of origin in a finite time, producing spurious correlations that would show up in $\hat{Z}(t)$ but would not be present in a large- N system. To see if this effect is relevant, we estimated the time it would take for an acoustic wave to cross the region, using the numbers from [1]. The speed of sound in sodium at its melting temperature is 2.5×10^5 cm/s, and the volume of the region occupied by one atom is $278 a_0^3$, so from the fact that there are 500 atoms one finds that the time required for an acoustic wave to cross the region is $783 \delta t$, or about 800 timesteps. (The speed of sound in sodium at our lower temperatures varies from that at the melting point by roughly 5%, so this result is valid to the same accuracy.) In the Figure below, the MD result for $\hat{Z}(t)$ begins to show small oscillatory revivals at about this time; we conclude that this is a finite size effect, but it does not affect the data before that time.

In Fig. 2, Eq. (15) is plotted on top of the MD data for $\hat{Z}(t)$ of sodium at the two temperatures. Although both temperatures compare exceptionally well to the harmonic theory, the match is visibly poorer for the lower temper-

ature. However, repeated MD runs at the lower temperature revealed that overall variations in $\hat{Z}(t)$ amount to 10^{-2} on average, which is the same order as the differences between theory and MD in this Figure. By 500 timesteps the theory is slightly out of phase with the MD data, and this small difference persists out to more timesteps.

4 Conclusions

These results show that the motion of a liquid in a single potential valley is harmonic to an extremely high approximation; the harmonic prediction for the function $\hat{Z}(t)$ matches the calculation from MD very closely. Any contributions due to anharmonicity (which are certainly present) are at most of the same order as the accuracy of the MD calculations.

Some form of harmonic approximation, such as the one used here, has been taken up by many workers attempting to understand the dynamics of liquids, and it is helpful to compare their models with our approach. One of the most popular is the theory of Instantaneous Normal Modes (INM), introduced by Rahman, Mandell, and McTague [6] and LaViolette and Stillinger [7] and developed extensively by Stratt (for example, [8]). Stratt expands the many-body potential in the neighborhood of an arbitrary point to second order in displacements from that point, and he expresses the potential as a quadratic sum of normal modes, in which the frequencies may be either real or imaginary. He then replaces the frequencies by their thermal averages over the potential surface, resulting in a temperature-dependent density of frequencies. From this point he calculates the system's motion and considers various time correlation functions, including $Z(t)$. He observes that his results are accurate to order t^4 for short times, but his predictions also diverge from MD results very rapidly, in a time shorter than half of one vibrational period. The agreement with MD at long times can be improved by omitting the imaginary frequencies from the calculation of $Z(t)$, but of course this makes the short time behavior inexact. (The work of Vallauri and Bermejo [9] follows Stratt's procedure.) Efforts to improve the long time behavior of the correlation functions calculated using INM have been made by Madan, Keyes, and Seeley [10], who have attempted to extract from the imaginary part of the INM spectrum a damping factor for $Z(t)$ of the general type suggested by Zwanzig [11]. Also taking their cue from Zwanzig, Cao and Voth [12] have followed a slightly different path, replacing the actual

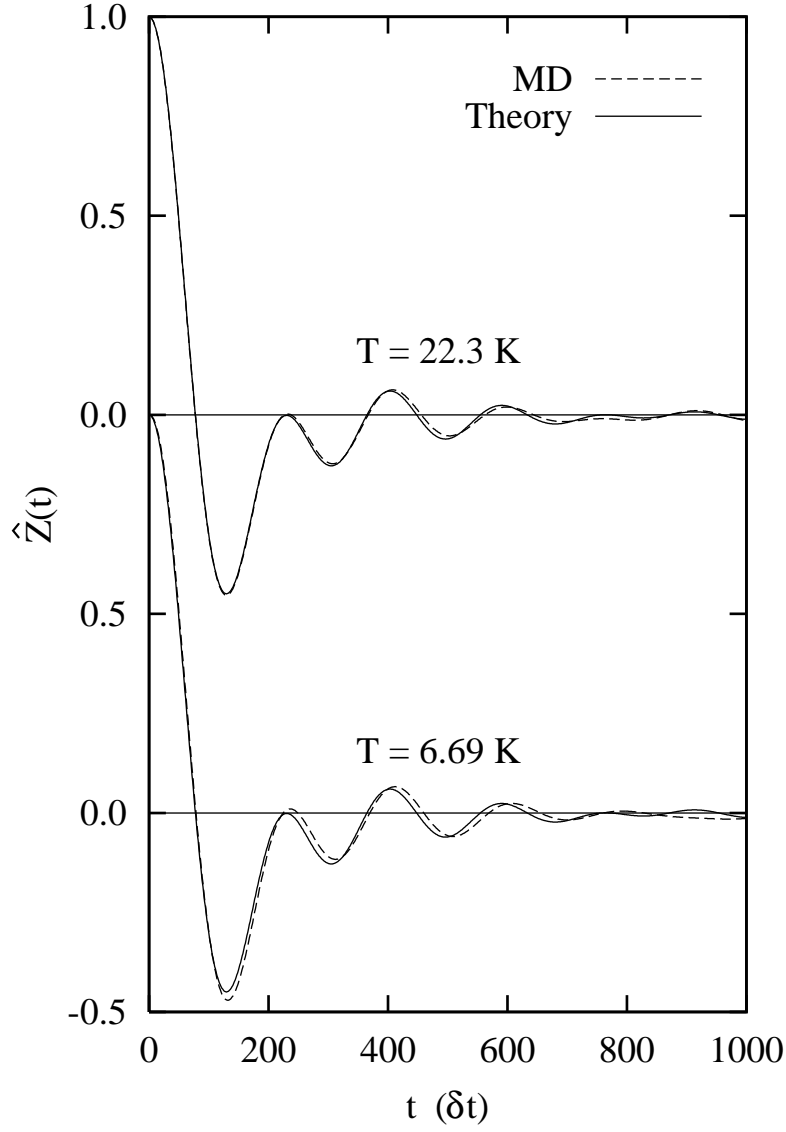


Figure 2: The theoretical prediction (Eq. (15)) for $\hat{Z}(t)$ of sodium moving in a single random valley compared with MD data at $T = 6.69$ K and $T = 22.3$ K.

potential by a set of temperature-dependent effective normal modes which, as they emphasize, bears little resemblance to the mechanical normal modes of a single many-particle valley. In fact, they state quite explicitly that a theory based on purely mechanical normal modes will have little success in accounting for equilibrium or dynamical properties of liquids.

An obvious difference between our theory and INM is the nature of our approximation. In INM, one approximates the potential quadratically at an arbitrary point, with the result that the motion so predicted is accurate only for very small times; in our theory, we expand the potential only at very special points where we know the predicted motion will be valid for very long times. Both theories then face the problem of extending their validity beyond the initial approximation, of course, and we will briefly mention our extension in the final paragraph below, but there is one particular reason why we strongly prefer the approach taken here: The other models all replace the true potential by a temperature-dependent potential determined by one or another thermal averaging process. A temperature-dependent potential does not provide a true Hamiltonian, and therefore it cannot be used to calculate the quantum or classical motion, i.e., it cannot be used in the Schrödinger equation or Newton’s law. (On the dynamical level, temperature is not even a well-defined concept.) Further, the Hamiltonian resulting from a temperature-dependent potential cannot be used to do statistical mechanics, except through uncontrolled self-consistent procedures. We prefer to build our theory in terms of the actual potential, hence in terms of its true Hamiltonian, and to find at least approximate solutions for the Hamiltonian motion, so we can apply the standard procedures of equilibrium and nonequilibrium statistical mechanics.

Further, we would argue that Cao and Voth’s skepticism regarding purely dynamical approaches is unfounded, given the results here. It is difficult to compare our $\hat{Z}(t)$ results to those of others, because their MD-simulated states are not always characterized as diffusing or nondiffusing. We are fairly confident that Vallauri and Bermejo’s Fig. 2b is a comparable state (glassy Cs at 20 K), and we believe our fit to MD is slightly better. Madan, Keyes, and Seeley’s Fig. 3b is an ambiguous case (it is likely that a glass transition has occurred), but there also we are confident that our match with MD is better. Hence we would claim that this method shows as much promise as the others currently available, and with the physical potential as opposed to a thermal average potential.

It is also instructive to compare the results of this paper with a model for

$\hat{Z}(t)$ previously proposed by Wallace [5] in which a single particle oscillates in a three-dimensional harmonic valley, and at each turning point it may with probability μ “transit” to an adjacent valley. To apply that model to a non-diffusing case, we set $\mu = 0$ (indicating no transits), yielding $\hat{Z}(t) = \cos(\omega t)$. Clearly this would not fit the MD data for any ω , and it is easy to see why: Wallace included only one frequency in his earlier model, whereas our Eq. (15) contains contributions from many frequencies, all of which are necessary to raise the first minimum in $\hat{Z}(t)$ above -1 and then damp $\hat{Z}(t)$ out by dephasing. This suggests an alternate path to understanding diffusing states: Begin with a mean atom trajectory model that by construction reproduces the correct result for $\hat{Z}(t)$ in the nondiffusing regime (Eq. (15)), and then incorporate Wallace’s notion of transits into this model. Our work in this direction, with comparison to MD data for higher-temperature diffusing states of liquid sodium, will be described in a subsequent paper [13].

References

- [1] D. C. Wallace and B. E. Clements, Phys. Rev. E **59**, 2942 (1999).
- [2] B. E. Clements and D. C. Wallace, Phys. Rev. E **59**, 2955 (1999).
- [3] D. C. Wallace, Phys. Rev. E **56**, 4179 (1997).
- [4] D. C. Wallace, Phys. Rev. E **58**, 1717 (1998).
- [5] D. C. Wallace, Phys. Rev. E **58**, 538 (1998).
- [6] A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. **64**, 1564 (1976).
- [7] R. A. LaViolette and F. H. Stillinger, J. Chem. Phys. **83**, 4079 (1985).
- [8] M. Buchner, B. M. Ladanyi, and R. M. Stratt, J. Chem. Phys. **97**, 8522 (1992).
- [9] R. Vallauri and F. J. Bermejo, Phys. Rev. E **51**, 2654 (1995).
- [10] B. Madan, T. Keyes, and G. Seeley, J. Chem. Phys. **94**, 6762 (1991).
- [11] R. Zwanzig, J. Chem. Phys. **79**, 4507 (1983).

- [12] J. Cao and G. A. Voth, J. Chem. Phys. **103**, 4211 (1995).
- [13] E. Chisolm and D. Wallace, submitted to Phys. Rev. E; cond-mat/0002058.